

## Ultrafast Na Intercalation Chemistry of $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$ Nanodots Planted in Carbon Matrix as a Low Cost Anode for Aqueous Sodium-Ion Batteries

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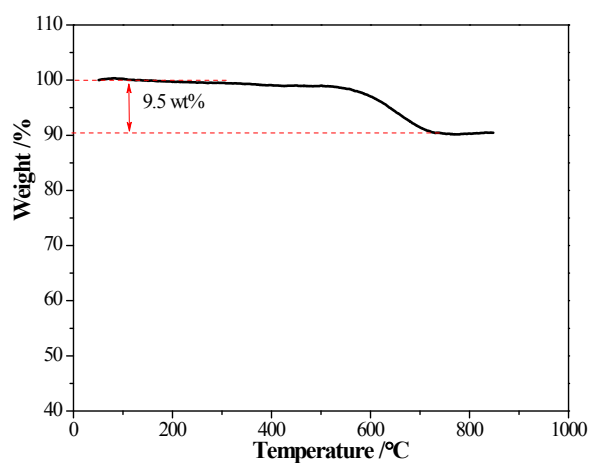
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### S1 Experimental section

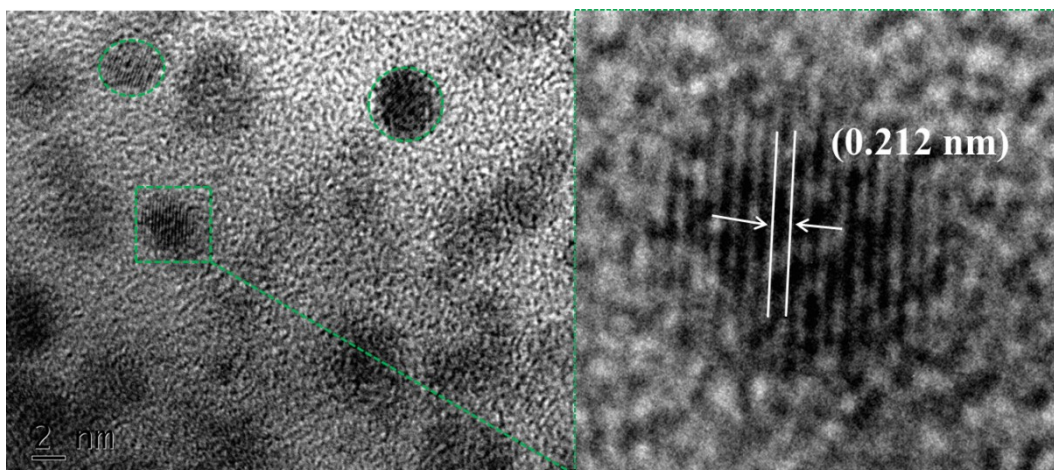
The  $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$  material was synthesized with a simple sol-gel route. In specific, a precursor solution was firstly prepared by dissolving 0.6890 g citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , 99.5%), 0.5296 g manganese acetate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , 99%), 0.7090 g sodium acetate ( $\text{CH}_3\text{COONa}$ , anhydrous, 99%), and 1.4912 g ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ , 99%) in 30 ml distilled water and then dropping the isopropyl titanate ethanol solution consisting of 2 ml  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$  (95%) and 3 ml  $\text{CH}_3\text{CH}_2\text{OH}$  (99.7%). After being sufficiently stirred, the precursor solution was evaporated at 75 °C until a gel was obtained, followed by drying the gel at 100 °C overnight. The resultant powder was treated at 450 °C for 4 h and 600 °C for 8 h in Ar-fluxing atmosphere.

X-ray diffraction (X'Pert Powder with a Cu  $K\alpha$  radiation source) was employed to confirm the crystal structure of the as-synthesized material, and the XRD pattern was recorded in the range of 10-70° with a scanning rate of 8°  $\text{min}^{-1}$ . The morphological properties were observed with scanning electron microscopy (JSM7500F) and transmission electron microscopy (JEM-2100). The practical composition involving element ratio and carbon content was determined by combining energy-dispersive spectrometer and thermogravimetric analysis (STA449F3, NETZSCH) with a heating rate of 5 °C  $\text{min}^{-1}$ .

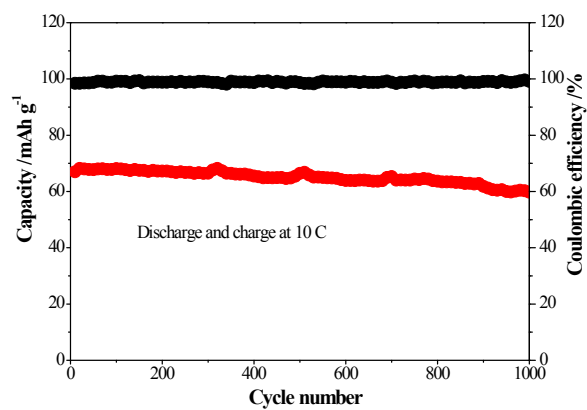
Electrochemical measurements were carried on a three-electrode system with NiHCF counter electrode, Ag/AgCl (saturated KCl) reference electrode, 6 M  $\text{NaClO}_4$  aqueous electrolyte and prepared working electrode. The working electrode consists of 70 wt% active material ( $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$ ), 20 wt% Super P carbon and 10 wt% PVDF binder. The loading of the active material in electrode is about 2.5  $\text{mg cm}^{-2}$ . The cyclic voltammetry was carried out on electrochemical workstation (CHI 600E) in the potential range of -1.0 and 0 V, while galvanostatic charge/discharge tests were performed between -1.0 and 0 V on Land Test System (CT2001A). In this work, the specific capacity is calculated based on the active  $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$ .



**Figure S1.** TG curve of the  $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$  material in air.



**Figure S2.** HRTEM images of the  $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$  material



**Figure S3.** Cycling performance of the  $\text{Na}_2\text{Ti}_{3/2}\text{Mn}_{1/2}(\text{PO}_4)_3$  material at 10 C.

**Table S1.** Performance comparison of reported anode materials for aqueous SIBs.

Material	Reversible capacity	Capacity retention
NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>1</sup>	~105 mAh g <sup>-1</sup> at 1 C	86% after 100 cycles (1 C)
Na <sub>3</sub> MgTi(PO <sub>4</sub> ) <sub>3</sub> <sup>2</sup>	54 mAh g <sup>-1</sup> at 0.2 C	94.2% after 100 cycles (0.5 C)
Na <sub>3</sub> MnTi(PO <sub>4</sub> ) <sub>3</sub> <sup>3</sup>	58.2 mAh g <sup>-1</sup> at 0.5 C	~97% after 100 cycles (1 C)
Na <sub>2</sub> TiV(PO <sub>4</sub> ) <sub>3</sub> <sup>4</sup>	52 mAh g <sup>-1</sup> at 1 C	94% after 500 cycles (5 C)
Na <sub>2</sub> Ti <sub>3/2</sub> Mn <sub>1/2</sub> (PO <sub>4</sub> ) <sub>3</sub> (this work)	78.8 mAh g <sup>-1</sup> at 0.5 C	93% after 200 cycles (1 C) 90% after 1000 cycles (10 C)

1. W. Wu, J. Yan, A. Wise, A. Rutt and J. F. Whitacre, *J. Electrochem. Soc.*, 2014, **161**, A561-A567.
2. F. Zhang, W. Li, X. Xiang and M. Sun, *Chem. Eur. J.*, 2017, **23**, 12944-12948.
3. H. C. Gao and J. B. Goodenough, *Angew. Chem. Int.*, 2016, **55**, 12768-12772.
4. H. Wang, T. Zhang, C. Chen, M. Ling, Z. Lin, S. Zhang, F. Pan and C. Liang, *Nano Res.*, 2017, **11**, 490-498.